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Re-analysis of the ultraviolet absorption spectrum of ozone

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A re-analysis of the Huggins and Hartley bands in the ultraviolet absorption spectrum of O₃ is presented in which the structure in both bands is assigned to vibrational progressions in the symmetric stretching mode ν_1 and the bending mode ν_2 but not the asymmetric stretching mode ν_3 . The present improved fit of a larger range of bands results in relatively large anharmonicity terms, whereas previous assignments have relied on the motion being largely harmonic in the upper state. From a consideration of the shape of single surface required to support both sets of vibrational data, it is concluded that the Huggins bands almost certainly terminate on the 2^1A_1 state rather than the 1^1B_2 state. © 2001 American Institute of Physics. [DOI: 10.1063/1.1412254]

I. INTRODUCTION

The weakly structured Huggins and Hartley bands of ozone are illustrated in Fig. 1 using the data of Molina and Molina.¹ The absorption is dominated by the bell-shaped Hartley band between 210 and 310 nm which is generally believed to be due to the electronically allowed transition $1^1B_2 \leftarrow X^1A_1$. It is well known that photolysis of the 1^1B_2 state over this wavelength range yields the spin allowed products $O(^1D) + O_2(^1\Delta_g)$ and $O(^3P_J) + O_2(X^3\Sigma_g^-)$. We have recently shown² that photolysis of the band system to lower energy, called the Huggins band, leads to the formation of, among other fragments, the spin-forbidden products $O(^3P_J) + O_2(b^1\Sigma_g^+)$. As an aid to better understanding the photodissociation of O₃ we have carried out a re-analysis of the absorption spectrum itself.

One key question that has not been answered with certainty is whether the Huggins band system is due to a transmission to the same upper electronic state as the Hartley band. This has a direct bearing on the vibrational assignment of the bands through vibronic symmetry arguments, but a broader question that is somewhat decoupled from the symmetry arguments concerns the number of bound levels of the asymmetric stretch mode, ν_3 , that are supported by the upper surface or surfaces. The coordinate q_3 associated with this mode leads to dissociation, and the number of bound levels in ν_3 provides information about the positions of surface crossings that, in turn, influence the energy disposal among the various dissociation and predissociation channels.

Fortunately, there is only one other electronic state which could be optically active in the region 30 000–45 000 cm⁻¹, i.e., the 2^1A_1 state. The transition $2^1A_1 \leftarrow X$ is forbidden with regard to the dominant electronic configurations, whereas the transition to the 1^1B_2 state is fully allowed. It is generally agreed that the potential energy surface (PES) of the 1^1B_2 state has a saddle point of C_{2v} symmetry (i.e.,

when $r_{12}=r_{23}$) and that the two equivalent minima on this surface are in the entrance and exit valleys leading to this saddle point (i.e., when the molecule has C_s symmetry). A PES for a fixed angle that summarizes the common features of all the calculations of the 1^1B_2 surface is sketched in Fig. 2: this surface is generated from the expansion coefficients reported by Leforestier *et al.*³ Individual calculations differ in the precise location of the minima and height and second derivatives of the saddle point.^{3–6} The 2^1A_1 surface, on the other hand, has a shallow minimum of C_{2v} symmetry at a more extended geometry than that of the ground state ($r_{12}=2.6 a_0$ compared to $2.4 a_0$) and at an energy approximately 0.5 eV below the minimum of the 1^1B_2 state.^{5,6} The 2^1A_1 state mixes with the 1^1B_2 state on distortion to C_s symmetry when both become A' . This allows the 2^1A_1 state to borrow intensity from the 1^1B_2 state through a transition dipole from the ground state that is linear in the asymmetric stretch coordinate q_3 .

In this paper we present a re-assignment of the vibrational structure of both the Huggins and Hartley band systems which recognizes the considerable anharmonicity that is to be expected on the weakly bound upper surface(s). In these new assignments, only progressions in ν_1 , the symmetric stretching vibration, and ν_2 , the bending vibration, are observed, as in the two earliest studies,^{7,8} but now all hot bands originate from one quantum of ν_1 in the ground state rather than from one quantum of ν_3 . These re-assignments produce a rather different picture of motion on the excited surface in the asymmetric stretch coordinate. Finally, the question of whether the two band systems terminate in the same upper state (1^1B_2) or on different states (1^1A_1 and 1^1B_2) is considered in the light of the re-assignment.

II. RE-ASSIGNMENT OF THE HUGGINS BAND

A. Previous assignments

Since the first study in the 1930's, the Huggins bands of O₃, observed between 310 and 360 nm, have been vibrationally analyzed in several different ways. Simons *et al.*⁷ agreed with the original, apparently simple, analysis⁸ in

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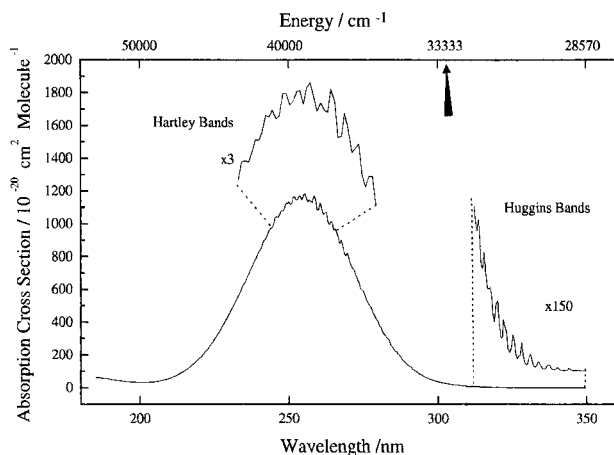


FIG. 1. The UV absorption spectrum of O_3 at 226 K (Ref. 1). The arrow indicates the (0,0) band of the Hartley system at $32\,926\text{ cm}^{-1}$. The (0,0,1) band of the Huggins system is off scale at $27\,112\text{ cm}^{-1}$.

which the spectrum was assigned as being made up of progressions in ν_1 and ν_2 , based on an electronic origin at 351.5 nm ($28\,450\text{ cm}^{-1}$). They also concluded that no vibrational progressions in ν_3 were observed. Brand *et al.*⁹ carried out an analysis using the data of Simons *et al.*,⁷ and based on the reported presence of ν_3 hot bands and a Franck-Condon analysis, deduced that the upper state has 1A_1 symmetry, in contrast to previous theoretical calculations¹⁰ which suggested that the Huggins bands and the Hartley continuum have the same upper state of 1B_2 symmetry. In their vibrational assignments,⁹ the position of the electronic origin remained unchanged and a long progression, up to $v=6$, in ν_1 was reported, while the maximum number of quanta of ν_2 and ν_3 were 1 and 2, respectively. Subsequently, Katayama¹¹ recorded low-temperature spectra of $^{16}\text{O}_3$ and $^{18}\text{O}_3$, from which he obtained isotope shifts and hence concluded that the electronic origin must be much lower in energy at 368.7 nm ($27\,124\text{ cm}^{-1}$), which corresponds to a shift of two quanta of ν_1 . However, apart from increasing the numbering of the ν_1 progression by two, Katayama agreed with the

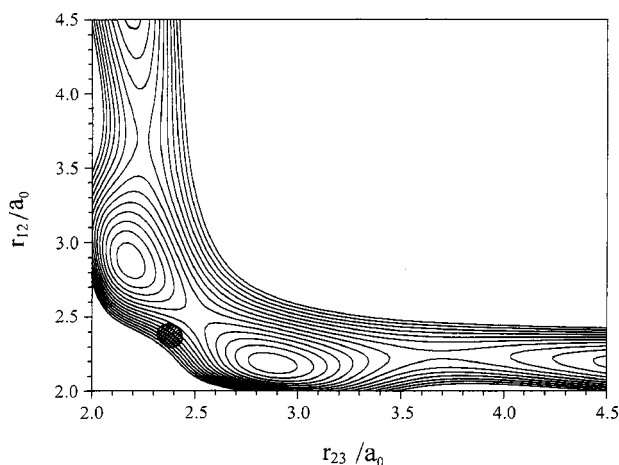


FIG. 2. A generic C_s representation of the 1^1B_2 surface. The shaded area represents the Franck-Condon window of zero-point motion in the ground state.

assignments of Brand *et al.*⁹ In the most recent study, Joens¹² argued that, since it was believed that the electronic state responsible for the Huggins bands has 1A_1 symmetry, an odd number of quanta of ν_3 , a b_2 vibration, must be excited in the upper state for a vibronic transition to be observed strongly. With this constraint, the spectrum was assigned as consisting of the same long progression in ν_1 , 0 or 1 quanta of ν_2 and a long progression in ν_3 (odd only). While the alternative analyses of Katayama¹¹ and Joens¹² both explain most of the experimental observations, the authors recognized that there are two significant features which are not adequately accounted for. First, in both overall assignments it was not possible to provide definitive assignments for peaks appearing at higher energy, i.e., above $32\,000\text{ cm}^{-1}$. It was suggested¹² that these bands were perturbed by a second electronic state. Second, all bands having one quantum of ν_2 excited are at least as intense as the equivalent bands with no ν_2 excitation, but surprisingly, no higher members of the progressions are observed. This phenomenon was explained¹² as being due to the existence of a barrier between $v=1$ and $v=2$ in ν_2 (i.e., a double minimum potential^{5,6}) and that no bound levels were observed above this barrier, perhaps because of an avoided crossing reached in the expanded range of the bond angle that opens up above the barrier.

B. The new assignment

There are three extensive experimental data sets which give the positions of the vibrational bands in the Huggins system available in the literature, those given by Brand *et al.*⁹ and Katayama¹¹ were obtained from their own experimental results, while that reported by Joens¹² was obtained from an analysis of the spectrum recorded by Freeman *et al.*¹³ The present analysis exclusively uses the data of Katayama¹¹ since it is the most extensive and also includes the equivalent data for $^{18}\text{O}_3$. The band positions are presented in Table I.

The current assignments of the cold bands, presented in Table I, are similar to those of Simons *et al.*⁷ in that the spectrum only contains extended progressions in ν_1 and ν_2 . The main difference is in the numbering of the ν_1 progression, which in the present analysis is taken from isotope studies¹¹ which predicted an unseen $v=0$ band around $27\,124\text{ cm}^{-1}$ and results in our numbering being two quanta higher than that given previously.⁷ Recently, Burrows *et al.*¹⁴ have recorded absorption spectra at temperatures between 200 and 300 K. In the spectrum¹⁵ recorded at 203 K, a cold band can be clearly observed around $27\,112\text{ cm}^{-1}$ and this is assigned as the $\nu_1\ v=0$ band.

The new assignments of part of the Huggins band are illustrated in the photofragment excitation (PHOFEX) spectrum of O_3 shown in Fig. 3. The spectrum was recorded by detecting $\text{O}(^3P_0)$ atoms by $\text{O}(3p^3P_0 \leftarrow 2p^3P_0)(2+1)$ resonance enhanced multiphoton ionization with a probe wavelength of 226.23 nm . The experimental details are given in Ref. 16 from which the figure is reproduced. It can be seen that, in this region, the intensities of the members of the ν_1 progression peak at $v=6$, while the intensities of the members of each ν_2 progression based on these false origins all

TABLE I. Assignment of the hot and cold band transitions (cm^{-1}) observed in the Huggins band absorption spectra of $^{16}\text{O}_3$ and $^{18}\text{O}_3$. Also given are the differences between the transition energies observed (Ref. 1) and those calculated using the constants given in Table III. The estimated experimental uncertainty is $\pm 7 \text{ cm}^{-1}$. The values for the ν_1 hot bands are calculated in the same way using $\omega_1''(^{16}\text{O}_3) = 1103 \text{ cm}^{-1}$ and $\omega_1''(^{18}\text{O}_3) = 1042 \text{ cm}^{-1}$. The assignments do not contain an assignment for the ν_3 mode for reasons discussed in the text.

ν_1, ν_2	$^{16}\text{O}_3$ cold band		$^{16}\text{O}_3$ hot band		$^{18}\text{O}_3$ cold band		$^{18}\text{O}_3$ hot band	
	Expt.	Expt.-Calc.	Expt.	Expt.-Calc.	Expt.	Expt.-Calc.	Expt.	Expt.-Calc.
0,0	27 112 ^{a,b}							
1,0	27 818 ^a							
1,1	28 169 ^a				27 799 ^a			
2,0	28 465	9	27 360 ^c	7		5		
1,2			27 415 ^c	-6	28 121 ^a			
2,1	28 803	-5			28 405	-2		
1,3			27 765	-4				
3,0	29 082	1	27 974	-4	28 727	-1		
2,2	29 146	-2	28 041	-4		-3	28 005	-1
1,4			28 094	-10	28 992		28 066	20
3,1	29 412	-1	28 305	-5	29 044	-6	28 257	-8
2,3			28 367	-5			28 313	-1
4,0	29 660	-7	28 555	-9	29 301	-6	28 500	-10
3,2	29 724	-9	28 620	-9		-2	28 563	-5
2,4			28 678	-10	29 546		28 625	13
4,1	29 974	-5	28 860	-15	29 607	1	28 804	-4
3,3	30 036	-4	28 935	-2		-1	28 860	-1
2,5			28 995	5	29 851			
5,0	30 209	-5			29 901	-1		
4,2	30 277	-1	29 165	-10		2	29 088	-8
3,4	30 329	-6	29 231	-1	30 076	1	29 146	3
5,1	30 509	4			30 140	-1		
4,3	30 570	5			30 186	8		
6,0	30 724	3			30 358	3		
5,2	30 790	6			30 423	2		
4,4	30 850	10			30 570	-1		
6,1	30 999	7			30 634	1		
5,3	31 059	8			30 682	1		
4,5	31 104	2			30 836	5		
7,0	31 193	3			30 894	10		
6,2	31 248	-4			30 945	-3		
5,4	31 309	3			31 035	1		
7,1	31 435	-6			31 090	-5		
6,3	31 486	-12			31 148	-15		
5,5	31 538	-10			31 272	-12		
8,0	31 616	-3			31 325	-9		
7,2	31 686	6			31 377	22		
6,4	31 756	24			31 439	16		
8,1					31 542	1		
7,3					31 593	-16		
6,5					31 686	3		
					31 736			
					31 807			

^aDenotes a weak or broad feature which was not included in the fitting procedure.

^bValue estimated from Ref. 15.

^cValue taken from Ref. 9.

show a smooth Franck-Condon envelope peaking between $\nu = 2$ and $\nu = 3$. These intensity distributions mirror those observed in the absorption spectrum which are presented in Table II.

The largest spacings in the ν_1 and ν_2 progressions are 696 and 351 cm^{-1} , respectively. These are much smaller than the ground-state frequencies¹⁷ of 1103 and 701 cm^{-1} . The spacings between the bands in the progressions in ν_1 and ν_2 are smoothly anharmonic, with the first quantum of ν_2 also smoothly decreasing as the quanta of ν_1 increase, as shown

in Table II. Both sets of observations are consistent with there being a large change in geometry between the ground and excited states, particularly with respect to q_1 .

Brand *et al.*⁹ proposed that the hot band data reported by Eberhardt and Shand, Jr.¹⁸ was not consistent with the analysis of Simons *et al.*⁷ with which the present analysis agrees in principle. The hot bands were assigned⁹ as being mainly due to a ground-state vibration of 1043 cm^{-1} which is the observed value¹⁷ for ν_3 . The positions of the hot bands in the spectra of $^{16}\text{O}_3$ and $^{18}\text{O}_3$ recorded by Katayama,¹¹ shown

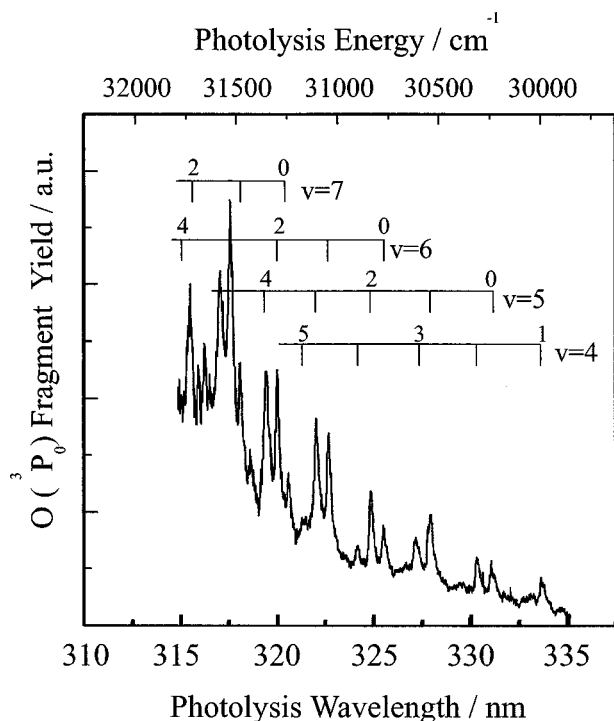


FIG. 3. The assignment of the PHOFEX spectrum for the $O(^3P_0)$ fragment yield detected following photolysis of O_3 in the Huggins bands between 29 850 and 31 750 cm^{-1} . The $O(^3P_0)$ fragments are detected by the $O(3p^3P_0 \leftarrow 2p^3P_0)$ (2+1) resonance enhanced multiphoton ionization transition with a probe wavelength of 226.23 nm. The ladders indicate the ν_2 progressions based on $v=4$ to $v=7$ of ν_1 .

in Table I, are effectively the same as those of the earlier study.¹⁸ It can be seen from the present re-assignments that all of the observed hot bands can also be interpreted as originating from ν_1 in the ground state which has a frequency of 1103 cm^{-1} (1040 cm^{-1} in $^{18}\text{O}_3$). No hot bands were assigned to transitions from ν_2 , despite the vibrational frequency being only 701 cm^{-1} . This is consistent with there

TABLE II. Observed separations (Ref. 1) (cm^{-1}) between, and relative intensity distributions (Ref. 12) of, the Huggins bands of $^{16}\text{O}_3$. The intensities are given in italics.

v	ν_1	$G_v - G_{v-1}$	ν_2 $G_v - G_{v-1}$				
			1	2	3	4	5
1	696	351					
					
2	647	338	343				
	...	<i>1</i>	<i>1</i>				
3	617	330	312	293			
	3	5	4	4	2		
4	562	314	303	293	280	254	
	10	16	18	16	12	8	
5	549	300	281	269	250	229	
	24	38	44	46	38	25	
6	515	275	249	238	270		
	28	48	50	46	12		
7	469	242	251				
	18	25	49				
8	423						
	12						

TABLE III. The vibrational constants (cm^{-1}) of the Huggins and Hartley bands obtained by fitting the band positions shown in Table III to Eq. (1) using a least-squares method.

	Huggins bands		Hartley bands	
	$^{16}\text{O}_3$	$^{18}\text{O}_3$	$^{16}\text{O}_3$	$^{18}\text{O}_3$
ω_1	752.3 ± 4.2	701.6 ± 4.8	927.7 ± 7.0	905.3 ± 7.8
ω_2	415.0 ± 5.1	376.7 ± 15.1	355.5 ± 15.1	321.5 ± 16.0
x_{11}	-19.5 ± 0.4	-16.9 ± 0.4	-23.2 ± 0.5	-23.6 ± 0.5
x_{12}	-20.2 ± 0.6	-15.2 ± 0.7	-8.3 ± 1.1	-7.9 ± 1.4
x_{22}	-6.2 ± 0.6	-5.1 ± 0.6	-4.0 ± 2.1	-1.6 ± 2.2
ν_{e0}	$26\,516.9 \pm 12.5$	$26\,583.9 \pm 13.2$	$32\,290.5 \pm 31.7$	$32\,358.4 \pm 34.8$
σ^a	7.4	7.6	28.6	39.1

^aStandard deviation of the calculated bands from the experimental values.

being a longer progression in ν_1 than in ν_2 in the cold band spectrum, both observations again suggest that there is a larger difference between the ground- and upper-state surfaces with respect to q_1 than to q_2 . The hot band assignments will be re-examined later following a discussion of the upper-state surface.

The band positions, ν , given in Table I were fitted to Eq. (1) using a least-squares fitting procedure and the resulting constants are presented in Table III.

$$\nu = \nu_{e0} + \omega_1(v_1 + 1/2) + \omega_2(v_2 + 1/2) + x_{11}(v_1 + 1/2)^2 + x_{12}(v_1 + 1/2)(v_2 + 1/2) + x_{22}(v_2 + 1/2)^2. \quad (1)$$

In Eq. (1), ν_{e0} will include one and a half quanta of ω_3 if the transition terminates on the 1A_1 surface.

The fit generated from these constants is very good in that the standard deviation of 7 cm^{-1} is the same as the estimated experimental uncertainty. One of the reasons for the goodness of the fit is that below 32 000 cm^{-1} the individual vibronic bands do not overlap significantly, in marked contrast to the peaks in the Hartley band structure. There are several strong broad bands between 32 000 and 33 000 cm^{-1} which have not been fully assigned in previous studies.^{11,12} Extrapolation of the assigned progressions in ν_1 and ν_2 in the present analysis show that these broad bands are due to the overlap of members of several different progressions which have become coincident because of the different anharmonicities of the progressions and are not resolvable at the experimental temperature of 195 K.¹³ However, these broad bands are at least partially resolved in an extension of the PHOFEX spectrum which covers the region between 316 and 298 nm (31 646 and 33 557 cm^{-1}).¹⁹ Unfortunately, the peak positions were not reported. The best estimates of the peak positions between 32 000 and 33 000 cm^{-1} , shown in Fig. 3 of Ref. 19, are compared with the calculated extrapolations of the ν_1 and ν_2 progressions in Table IV. There is a very good agreement between the experimental and calculated band positions, especially in view of the relatively large uncertainties in the estimates of the experimental values and in the errors associated with calculating values from an extrapolation. It was possible to further extend the assignment to include all of the observed peaks up to that of highest energy at 33 520 cm^{-1} , which is the (12,3) band.

TABLE IV. A comparison of the extrapolated Huggins band energies (cm^{-1}), calculated using the constants reported in Table III, with the observed 195 K absorption bands (Ref. 11) and the jet-cooled PHOFEX bands (Ref. 19).

ν_1, ν_2	$^{16}\text{O}_3$			$^{18}\text{O}_3$	
	Expt. (absorption at 195 K)	Expt. (PHOFEX jet-cooled)	Calc.	Expt. (absorption at 195 K)	Calc.
8,1	31 898	31 832	31 850	31 686	31 685
7,3	31 898	31 888	31 906	31 736	31 752
6,5	31 898	31 939	31 954	31 807	31 804
9,0		32 015	32 010		31 838
8,2	32 108	32 051	32 069	31 942	31 912
7,4	32 108	32 103	32 120	31 942	31 947
9,1	32 224	32 201	32 220		32 060
8,3	32 224	32 258	32 275	32 156	32 129
10,0	32 373	32 383	32 361	32 156	32 193
9,2	32 446	32 452	32 419	32 266	32 272
8,4	32 446	32 495	32 469	32 357	32 336
10,1	32 625 ^a	32 595	32 551	32 409	32 400
9,3	32 625 ^a	32 648	32 605		
11,0	32 625 ^a	32 712	32 673		
10,2		32 776	32 729		
11,1	32 900 ^a	32 889	32 843		
10,3	32 900 ^a	32 954	32 895		
12,0	32 900 ^a	33 031	32 946		

^aBand position estimated from Fig. 1 of Ref. 12.

If a progression in ν_3 in the Huggins bands is indeed absent, then this points to a predissociation by a repulsive state that intersects the upper surface along a seam at extended values of r_{12} and r_{23} . Hay *et al.*²⁰ have proposed that a 1A_1 surface (the *R* state), correlating with $\text{O}(^3P_1)$ and $\text{O}_2(X^3\Sigma_g^-)$, crossing the nearly converged 1B_2 and 2^1A_1 surfaces at $r_{ij} \approx 3.2$ a.u., causes this predissociation. If the upper state has B_2 symmetry, then only the zero point motion in the wells lies below the crossing: If it has A_1 symmetry, then $v=0, v=1$, and possibly, $v=2$ of ν_3 are bound because a $\Delta v=1$ transition is required by the B_2 symmetry of the transition dipole.

Thus far, no assumptions have been made, or conclusions drawn, about the symmetry of the upper state responsible for the Huggins bands. These points will be addressed in Sec. IV following a re-assignment of the Hartley band vibrational structure.

III. RE-ASSIGNMENT OF THE HARTLEY BANDS

A. Previous assignments

Only two assignments of the Hartley band vibrational structure have been reported. In the first, Joens²¹ carried out an analysis using previously recorded experimental spectra.^{1,7,13,22,23} In this, the underlying Hartley continuum was first subtracted leaving only the structured portion. The assignment included long progressions in ν_1 , $v=0-8$, and shorter progressions in ν_2 , $v=0-5$, which were essentially harmonic with vibrational spacings of 1108 and 298 cm^{-1} , respectively. An attempt to resolve the uncertainty in the absolute numbering of both bending and symmetric stretching progressions given in this study was made by Parisse *et al.*²⁴

They recorded the absorption spectra of both $^{16}\text{O}_3$ and $^{18}\text{O}_3$ and analyzed them using the same method as Joens.²¹ The observed isotope shifts were used to confirm the vibrational numbering proposed in the earlier study.

Both studies contained several anomalous observations. First, the fits of the experimental data gave standard deviations which were approximately three times larger than the estimated precision of the band positions. Furthermore, the assignments were unable to explain the intensity alternation along the bending progressions based on certain quanta of symmetric stretch or the large variation in the observed band widths. Finally, the calculated anharmonicity parameter for the bending vibration had, unusually, a small but significant positive value.

B. The new assignment

The band positions given by Parisse *et al.*²⁴ are used exclusively as the experimental data set in the present study. The observed band positions of $^{16}\text{O}_3$ and $^{18}\text{O}_3$ are presented, together with their new assignments, in Table V. The spectrum is interpreted as being made up of short ν_2 progressions of up to six members based on a long progression of around eleven quanta of ν_1 .

The current assignment differs from those in the earlier studies in two respects: the symmetric stretching frequency is ca. 900 cm^{-1} rather than 1100 cm^{-1} and both ν_1 and ν_2 are very anharmonic. The most significant result of these two changes to the assignment is that almost all of the observed experimental peaks are comprised of at least two overlapping vibronic bands, hence neither the position nor the intensity of each individual vibronic band can be measured very accurately. In contrast, every peak observed in the Huggins bands up to that labeled (8,0) is a single vibronic band and the spacings and intensities of bands along any progression can be determined quite accurately. It should be noted that the spacing of 1100 cm^{-1} observed throughout the Hartley band spectrum and previously assigned^{21,24} to one quantum of ν_1 is approximately equal to one quantum of ν_1 plus one quantum of ν_2 in the present analysis.

The numbering of the vibrational progressions is very problematical. In the spectrum of the Huggins bands, equivalent pairs of vibronic bands of $^{16}\text{O}_3$ and $^{18}\text{O}_3$ could be unambiguously identified and hence the vibrational numbering could be easily calculated. As a result of the large number of overlapping features in the Hartley band spectrum, these pairs of bands cannot be uniquely identified with such certainty. The approach used here was to assume that, in the low-energy region of the spectra of the two isotopic species, each peak in the $^{16}\text{O}_3$ spectrum was paired with that nearest in energy in the $^{18}\text{O}_3$ spectrum and given the same vibronic assignment, i.e., in agreement with the analysis of Parisse *et al.*²⁴ If this assumption is correct, the relatively high frequency of ν_1 means that the proposed numbering of the ν_1 progressions should be quite certain.

The numbering of the ν_2 progressions are much less certain because of the lower frequency of ν_2 . Joens²¹ assigned three bands as (2,0), (3,0), and (4,0) as he could not identify any bands shifted to low energy of them by one

TABLE V. Assignment of the cold band transitions (cm^{-1}) observed in the Hartley band absorption spectra of $^{16}\text{O}_3$ and $^{18}\text{O}_3$. Also given are the differences between the transition energies observed (Ref. 24) and those calculated using the constants given in Table III. The estimated experimental uncertainty is $\pm 10 \text{ cm}^{-1}$. The assignments do not contain an assignment for the ν_3 mode for reasons discussed in the text.

ν_1, ν_2	$^{16}\text{O}_3$		$^{18}\text{O}_3$	
	Expt.	Expt.-Calc.	Expt.	Expt.-Calc.
0,3	33 908	-21	33 833	-63
1,0			33 833	15
0,4	34 152	-96	34 108	-93
1,1	34 152	17	34 108	-16
0,5			34 446	-56
1,2	34 440	-22	34 446	19
2,0	34 613	-18	34 516	-8
1,3	34 798	17	34 749	22
2,1	34 943	-14	34 925	2
1,4	35 096	5	35 049	26
2,2	35 273	-3	35 198	-20
1,5	35 409	15	35 359	43
3,0	35 409	-6	35 359	25
2,3	35 569	-17	35 467	-43
3,1	35 722	-11	35 608	-67
2,4	35 868	-21	35 773	-25
3,2	36 038	-6	35 979	17
2,5	36 187	4		
4,0			36 166	70
3,3	36 375	29	36 166	-80
4,1			36 381	2
3,4	36 669	29		
4,2	36 758	-7	36 632	-26
5,0	36 874	30	36 789	28
4,3	37 047	-11	36 928	-6
5,1	37 182	36	37 073	37
4,4	37 325	-19	37 187	-20
5,2	37 519	80	37 348	40
6,0	37 519	30	37 380	-31
4,5	37 624	2		
5,3	37 783	58	37 615	39
6,1	37 783	1	37 615	31
4,6			37 739	4
5,4	37 975	-27		
7,0	38 091	3	37 939	-11
6,2	38 091	23	37 939	29
6,3	38 332	-13	38 238	68
7,1	38 332	-41	38 238	29
8,0	38 624	-22	38 478	5
6,4	38 624	14	38 478	51
7,2	38 624	-22	38 478	14
6,5			38 652	-29
8,1	38 873	-44	38 754	30
7,3	38 873	-45	38 754	37
8,2	39 138	-47	38 920	-52
9,0	39 138	-8	38 920	-29
7,4	39 138	-41	38 920	-46
8,3	39 409	-36	39 182	-35
9,1	39 409	-5	39 182	-11
9,2	39 694	20	39 422	-10
8,4	39 694	-4	39 422	-36
9,3	39 989	63	39 645	-24
10,2	40 150	33	39 860	15
9,4	40 150	-20	39 860	-42
10,3	40 397	37	40 169	95
11,2			40 169	-42
11,3	40 718	-30	40 361	71
10,4			40 361	61
11,4	41 000	24		
12,2			40 562	32

quantum of bend. However, in the data presented by Parisse *et al.*,²⁴ the positions of bands assignable to three lower-energy bands were tabulated. These data appear to contain only one band of at least medium intensity, which does not have an associated band shifted by one quantum of ν_2 to lower energy, and this occurs at $36\,789 \text{ cm}^{-1}$ in the spectrum of $^{18}\text{O}_3$. In the present re-assignment, all bending quanta in the spectra of both isotopic species are numbered relative to this one band. Thus, although the relative numbering of the bending quanta appears to be well-established, the absolute numbering must remain more uncertain.

The assignment of bands below $41\,000 \text{ cm}^{-1}$, given in Table V, were fitted to Eq. (1) as before, with ν_{e0} being the energy of the saddle point, and the resulting constants are presented in Table III. When bands above $41\,000 \text{ cm}^{-1}$ were included in the experimental data set, there was a distinct deterioration in the overall fit. The most likely cause of this observation is that it is not possible to fit such an anharmonic progression as that of ν_1 above $v=10$ using only a second order Dunham expansion. The precision of the line positions does not warrant a higher-order fit unless careful consideration is given to the weighting of the additional data, otherwise, as has been observed elsewhere,²⁵ the lower order coefficients will become unrealistic.

While the standard deviation of the overall fit is still around 30 cm^{-1} , compared to the estimated experimental uncertainty of $\pm 10 \text{ cm}^{-1}$, the present assignment does have a significant advantage over the alternatives reported previously.^{21,24} Many of the observed peaks now consist of two or more overlapping bands which can explain the relatively poor fit. The same phenomenon of overlapping bands also explains why the intensities and widths of the bands belonging to what was originally assigned as a single progression vary so much and so irregularly.

The intensities of the observed bands of $^{16}\text{O}_3$ have been estimated by Joens.²¹ As a result both of the blending of individual vibronic bands to form the observed bands, and the inevitable errors involved in initially subtracting a large continuum background from the observed spectrum, it is not possible to gain as much quantitative intensity information on the Hartley bands as it was on the Huggins bands. However, qualitatively, it appears that the ν_1 and ν_2 progressions peak around $v=8$ and $v=3$, respectively.

IV. IMPLICATIONS OF THE PROPOSED RE-ASSIGNMENT FOR THE UPPER STATE PES

A. Simulation of the Hartley band absorption spectrum

Two different approaches have been used previously in attempts to simulate the Hartley band absorption spectrum. In the first, a wave function is propagated on a known excited-state surface and its development with time followed. The absorption spectrum is then obtained from the Fourier transform of the autocorrelation function. Numerous investigations have been carried out using this method and most of these are reviewed in Ref. 26. Subsequently, two further studies have been reported,^{27,28} one on each of the two most commonly used upper-state surfaces, the LLYM³ and the SW⁴. In both, simulations of the relative intensities

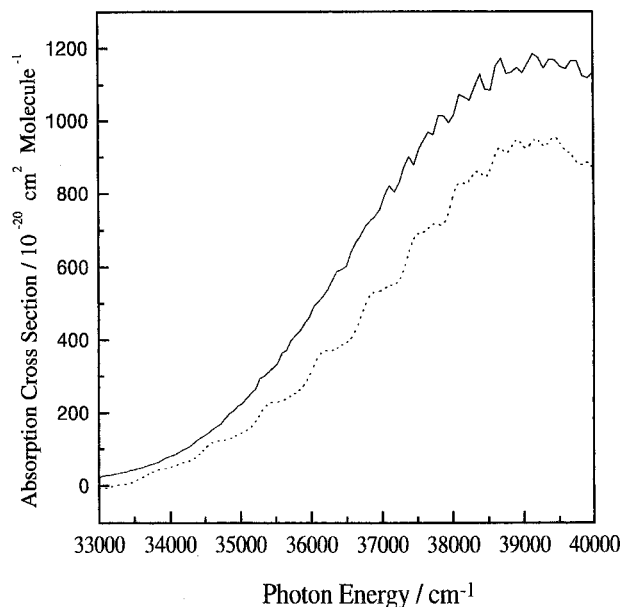


FIG. 4. Part of the UV absorption spectrum of O_3 . The full line shows the experimental spectrum (Ref. 1) at 226 K and the dotted line is the approximate reproduction outlined in the text.

of the broad continuum and the weak oscillatory structure superimposed on it were reproduced. However, no attempt was made to compare the positions of the calculated oscillatory maxima with those in the experimental spectrum.

The second approach uses the vibrationally adiabatic model of Pack.²⁹ The structure arises from bound motion in the symmetric stretch coordinate across the saddle point and in the bending mode and the energy width of each (ν_1, ν_2) line is that of the bound-continuum overlap integral in the asymmetric stretch coordinate. The two factors which govern the overall shape of the Hartley band absorption when using this latter model are the density of ν_1 and ν_2 levels of the upper 1B_2 state and the shape of the barrier between the two C_s minima, which is characterized by the second derivative with respect to q_3 at the saddle point, $-k'_{33}$. The ratio k'_{33}/k''_{33} , designated χ by Atabek *et al.*,³⁰ where k''_{33} is the force constant of the asymmetric stretch in the ground state, determines the range of energy on the upper surface covered by the amplitude of q_3 , while executing the zero-point motion in the ground state. Attempts to simulate the Hartley bands by Atabek *et al.*³⁰ and by Adler-Golden³¹ assumed an harmonic progression of both ν_1 and ν_2 modes and hence, the density of peaks used in these calculations was low. To compensate for this, k'_{33} had to be increased to a value slightly greater than that in the ground state. This effort to reproduce the overall width of the Hartley continuum had the effect of causing the structure to disappear almost entirely as it did in the calculation of Johnson and Kinsey.³²

We have applied this latter method to the vibrational analysis of the Hartley band outlined in Table V. In our fit, the anharmonicities of the modes is such that the density of the ν_1 and ν_2 levels is much higher than the previous harmonic models suggest. The inclusion of anharmonicities in the ν_1 and ν_2 modes is an essential consideration in any successful attempt to analyze the Hartley band using the

Franck-Condon model outlined previously. As an illustration of this, the Hartley band absorption can be reproduced in an approximate fashion by assuming that the q_3 peak with which each (ν_1, ν_2) peak is convoluted can be represented by a Lorentzian peak. The optimum match was obtained using widths of 430 cm^{-1} . This corresponds to a value of the χ parameter of Atabek *et al.*³⁰ of $\sim 1/4$ as judged from Fig. 1 of their paper. The positions of the (ν_1, ν_2) peaks are calculated using the fitted constants in Table III and their intensities are given by simple Gaussian envelopes in each of the two modes. The results are compared with the 226 K absorption data of Molina and Molina¹ in Fig. 4.

Although a gross oversimplification of the problem, this interpretation does illustrate that, once anharmonicities are included, it is possible for structure to survive and the overall width of the Hartley system to be preserved with a smaller (and more physically meaningful) value of k'_{33} , for the upper surface than for the ground state, in keeping with the smaller values of k'_{22} and k'_{11} . The diffuse structure of the Hartley bands is thus assigned to quasi-periodic orbits executing motion in the q_1 and q_2 coordinates across the saddle point. That structure is resolvable at all must mean that there are several recurrences before the wave packet created on the upper surface descends into the valleys and the molecule dissociates.

B. One or two upper state surfaces

There is still much controversy as to whether the Huggins band transitions terminate on the 1^1B_2 surface^{33–35} or the 2^1A_1 surface.^{5,12,36} In the light of our vibrational reassignments, we can now address the question of whether a single upper-state surface can be responsible for both the Hartley and Huggins band absorptions.

In our vibrational analysis, the structure seen in the Hartley band absorption has an unobserved origin corresponding to zero-point motion at the saddle point on the 1^1B_2 surface. It is possible to evaluate the energy of this saddle point relative to the ground state once an assignment has been made. Our assignment begins with the peak at $33\,908 \text{ cm}^{-1}$, assigned as (0,3), leading to a saddle point, corresponding to $(-1/2, -1/2)$, at $32\,291 \text{ cm}^{-1}$. This leads to the saddle point being at almost exactly the same energy as the dissociation limit and consequently to the minima of the C_s wells (i.e., located by the origin of the Huggins bands) being approximately 5000 cm^{-1} below both of the first two points. The few limitations to the accuracy of these points include the possibility that the saddle point should be lower due to unobserved Hartley band features to the red in the absorption spectrum.

The saddle point and a potential minimum (or equivalent minima) that come from our re-assignment may or may not be on the same surface. If we assume that they are both on the 1B_2 surface, then their absolute energies can be referenced to the dissociation limit of that surface, the $\text{O}(^1D) + \text{O}_2(a^1\Delta_g)$ channel, and the three points compared with *ab initio* surface calculations. This is done in Table VI, where the comparison is made with the SW,⁴ LLYM,³ and BPG⁶ surfaces. We can also compare calculated vibrational fre-

TABLE VI. A comparison of the parameters (cm^{-1}) which characterize previous *ab initio* 1^1B_2 surfaces with those of a single surface which would result from the present Huggins and Hartley band re-assignments.

Surface	Vibrational frequencies in C_s wells			Saddle point ^a	Well depth ^b
	ω_1	ω_2	ω_3		
LLYM (Refs. 3, 34, 35)	743.5	440.6	800.2	2500 ^d	687
SW (Refs. 4, 34)				8000 ^c	5500 ^c
BPG (Ref. 6)	770	612	586	2500 ^e	-180
Present work	752.3	415.0		5191 \pm 50	5215 \pm 20

^aThe saddle point between the C_s wells relative to the (0,0,0) level in the C_s wells.^bThe (0,0,0) level in the C_s wells relative to the $O(^1D) + O_2(a^1\Delta_g)$ dissociation limit.^cEstimated from Fig. 1 of Ref. 34.^dEstimated from Fig. 2 of Ref. 34.^eEstimated from Fig. 5 of Ref. 6.

quencies in the C_s wells with those from our assignments, although this does not bear directly on the question of one surface or two.

There have been two calculations reported that determine the vibrational levels supported by the C_s wells of the LLYM surface.^{34,35} The calculated vibrational frequencies match those of the Huggins bands quite closely and it was concluded that this single surface could be responsible for both the Huggins and Hartley bands. However, there appear to be some anomalies in such a conclusion. In the first study,³⁴ the upper-state surface was shifted vertically until the best agreement between the calculated and observed vibrational spacings and intensities was achieved. This optimized shift places the $O(^1D) + O_2(a^1\Delta_g)$ dissociation limit several thousand wave numbers below its known value. In addition, the best agreement was obtained when the position of the first calculated line was adjusted to the observed (2,0,0) band. If it is assumed that the first calculated line is really the (0,0,0) band, the surface must be shifted to even lower energy to achieve a correct match. In the second study,³⁵ the dissociation limit of the LLYM surface was fixed to the experimental $O(^1D) + O_2(a^1\Delta_g)$ dissociation limit and it was calculated that the (0,0,0) Huggins band should appear around 32 000 cm^{-1} , whereas the observed band origin lies around 27 000 cm^{-1} . While *ab initio* calculations are not at their most reliable when calculating dissociation energies, this simple comparison of the two points which define the well depth, one derived from the Huggins bands and the second from the asymptotic energy, strongly suggests that a surface similar to the LLYM surface cannot be responsible for the Huggins bands. The same argument applies to the surface calculated by Banichevich *et al.*⁶

In contrast, the well depth of the SW surface is consistent with the present analysis. However, several other characteristics of this surface appear to rule out the possibility that it could be responsible for both the Huggins and Hartley bands. First, the internuclear distances in the C_s wells are well outside the Franck-Condon region of the ground state. Second, the saddle point, which defines the origin of the Hartley system, is more than 8000 cm^{-1} above the bottom of the C_s wells which defines the origin of the Huggins system. Our analysis indicates that this spacing is around 5000 cm^{-1} . Finally, the model that we have used to interpret the Hartley

bands, where the molecule undergoes several vibrations orthogonal to the saddle point before dissociation, points to the dissociation pathway being very shallow. However, the curvature, $-k_{33}$, at the saddle point on the SW surface, is very large. Thus, while it is still possible that a new surface could be generated, which accounts for these discrepancies, the present analysis strongly points to the two bands terminating on different surfaces; the Hartley band on the 1^1B_2 and the Huggins on the 2^1A_1 .

C. An alternative hot band assignment

If, as seems likely, the Huggins bands terminate on the 2^1A_1 surface, the hot band assignments must be briefly reconsidered. While those assignments given in Table I remain valid, an alternative set of assignments becomes possible in the case of a 1A_1 upper state, since all of the cold band transitions terminate on levels containing one quantum of ν_3 . While the ν_1 and ν_2 hot bands of each of these transitions may be observed, the ν_3 hot band cannot since $\Delta v = 1$ for ν_3 must hold. Conversely, the ν_3 hot bands can only terminate on upper-state levels with an even number of quantum of ν_3 , levels which cannot be observed in cold band transitions. However, knowing the values of ν_3 in the ground state, 1042 and 985 cm^{-1} for $^{16}\text{O}_3$ and $^{18}\text{O}_3$, respectively,¹⁷ and by estimating a value for ν_3 in the upper state, an alternative set of hot band assignments were made and are shown in Table VII. The cold and hot band transition terminate on one and zero quanta of ν_3 in the excited state, respectively. The values of one quantum of ν_3 in the upper state in combination with each (ν_1, ν_2) vibrational level, which result from the assignments, are quite similar to those of ν_1 and are also shown in Table VII. The decrease in these values, as the associated number of quanta of ν_1 and ν_2 increases, is entirely consistent with trends seen in the cold bands. The isotope shifts also appear to be reasonable. At present, both sets of hot band assignments seem equally possible.

V. CONCLUSION

The discrete vibronic structure in both the Huggins and Hartley bands has been re-assigned to progressions in the ν_1 and ν_2 modes with either zero or one quanta of ν_3 . The values for ν_1 and ν_2 are now similar in the two bands and

TABLE VII. Alternative assignment of the hot band transitions (cm^{-1}) observed (Ref. 11) in the Huggins band absorption spectra of $^{16}\text{O}_3$ and $^{18}\text{O}_3$ in which $\nu''=1$ for ν_3 . It is assumed that $\Delta\nu=1$ for ν_3 and hence the cold and hot band transitions terminate on one and zero quanta of ν_3 , respectively. The values of ω_3 in the upper state in combination with each (ν_1, ν_2) level resulting from the assignment are calculated using $\omega_3(^{16}\text{O}_3)=1042\text{ cm}^{-1}$ and $\omega_3(^{18}\text{O}_3)=985\text{ cm}^{-1}$ are also given.

ν_1, ν_2	$^{16}\text{O}_3$			$^{18}\text{O}_3$		
	Cold band	Hot band	ω_3	Cold band	Hot band	ω_3
0,0	27 112					
1,0	27 818			27 799		
1,1	28 169			28 121		
2,0	28 465			28 405		
2,1	28 803			28 727		
3,0	29 082	27 360	680	28 992		
2,2	29 146	27 415	689	29 044		
3,1	29 412			29 301		
2,3		27 765				
4,0	29 660	27 974	644	29 546		
3,2	29 724	28 041	641	29 607	28 005	617
2,4		28 094			28 066	
4,1	29 974	28 305	627	29 851	28 257	609
3,3	30 036	28 367	627	29 901	28 313	603
5,0	30 209	28 555	612	30 076	28 500	591
4,2	30 277	28 620	615	30 140	28 563	592
3,4	30 329	28 678	610	30 186	28 625	576
5,1	30 509	28 860	607	30 358	28 804	569
4,3	30 570	28 935	593	30 423	28 860	578
3,5		28 995				
6,0	30 724			30 570		
5,2	30 790	29 165	583	30 634	29 088	561
4,4	30 850	29 231	577	30 682	29 146	551

significantly lower than in previous fits. The major changes to the previous assignments are the relatively large anharmonicity in the ν_1 mode, the inclusion of double assignments for many of the features due to overlapping bands, and the absence of a progression in ν_3 . The important implications of this anharmonicity and the increased density of levels for Franck–Condon models of the Hartley bands is also demonstrated by modeling the absorption with a width assigned to each vibrational band that is considerably less than that used in previous simulations and more in keeping with a generally flatter portion of the upper-state surface that is explored in the bound modes.

The question of whether the ultraviolet absorption of O_3 terminates on one or two upper electronic states is addressed by a comparison of the shape of the single surface required to support both sets of vibrational data with *ab initio* calcu-

lations of the 1^1B_2 surface, which is known to be responsible for the Hartley band. Serious inconsistencies between the shape of these potentials lead to the conclusion that the Huggins bands almost certainly terminate on the 2^1A_1 state rather than the 1^1B_2 state.

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